

## CALCULATION OF POLYTHERMAL SECTIONS OF TERNARY PHASE DIAGRAMS BY THE CONVEX HULL METHOD

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### ABSTRACT

An algorithm for ternary phase diagrams polythermal sections assessment based on the convex hull method has been suggested. It is based on  $p, T$ -sections set calculation in the needed temperature interval with step between them depending on required accuracy and its subsequent analysis. Improvements of existing technique of ternary isobaric-isothermal sections construction implemented in TernAPI software complex also have been proposed and successfully tested. Suggested modifications improve reliability of diagram regions discrimination near the singular points such as eutectic or peritectic and greatly increase the performance of  $p, T$ -sections construction. Polythermal sections of Au-Bi-Sb, Al-Mg-Zn, LiF-LiCl-LiI and another ternary systems have been calculated.

### INTRODUCTION

Phase diagrams assessment is an actual part of modern theoretical materials science. Most of modern programs for calculating multicomponent diagrams are based on the conditional minimization of Gibbs energy of the system. The sensitivity of this method to the initial approximation and to features of used minimization algorithm significantly complicates its practical application. Such situation makes a development of alternative methods for phase equilibria assessment, e.g. geometric, an actual problem. A rather new convex hull method belongs to them.

The convex hull method is based on the fact that equilibrium Gibbs energy ( $G$ ) surface of the system in extensive thermodynamic coordinates (e.g. amounts of components  $n_i$ , volume  $V$ , etc.) is the convex hull of  $G$  functions of all set of phases. It has a number of advantages: doesn't require specifying initial conditions, applicable for wide range of thermodynamic models, doesn't use explicit minimization of thermodynamic potentials [1]. It should be noted that convex hull method allows direct calculations of phase diagrams in extensive variables only ( $n_i$ , volume  $V$ , etc.).

For isobaric-isothermal sections of ternary systems this method is implemented in the TernAPI program developed at the Laboratory of Chemical Thermodynamics of MSU Chemistry Department [2]. However in the practical, e.g. industrial, applications an assessment and visualization of polythermal sections and surfaces (i.e. diagrams in extensive coordinates that cannot be obtained by the convex hull method directly) are often required.

So the technique of making polythermal sections of ternary phase diagrams using convex hull method was suggested and implemented into TernAPI package.

### POLYTHERMAL SECTIONS CONSTRUCTION METHOD

The proposed method of polythermal sections construction is based on the assessment of the  $p, T$ -sections set within specified range of temperatures with their subsequent analysis and consists of the next steps:

- (1) The set of phase diagram  $p, T$ -sections in the temperature range from  $T_{\min}$  to  $T_{\max}$  with user defined step  $\Delta T$  is constructed. All sections have the same resolution in components molar fractions coordinates ( $x_2, x_3$ ).
- (2) The cutting plane parallel to  $T$  axis and intersecting AB (A and B are the points inside the Gibbs-Rosebom triangle) interval in each composition triangle is plotted.
- (3) The rasterization of each  $p, T$ -section obtained in item 1 is carried out. Points situated on the interval AB are selected from each rasterized section. Phase composition of every point is stored in the matrix, in which every row corresponds to one temperature  $T_i$  and a column – to a definite composition  $\xi_i$ .
- (4) Based on the matrix from item 3 coordinates of boundaries between diagram areas are determined.
- (5) Using obtained data array the phase diagram polythermal section in the  $T$ - $\xi$  coordinates (temperature-composition) is plotted.

Suggested algorithm is implemented as the computer program in MATLAB programming language and uses the TernAPI kernel to calculate single  $p, T$ -sections. It comprise four modules – PolyTSection, CalcPolyTDiagram, BuildPolyTSection and ShowPolyTSection, which perform next functions:

- (1) First one (PolyTSection) is designed to setup user input data (path to the source file with information about system, temperature interval for section calculation, composition and temperature step, geometrical parameters of required polythermal section) and to call other three modules.
- (2) Second one (CalcPolyTDiagram) calculates the set of  $p, T$ -sections and determines phase composition and boundaries inside each of them.
- (3) Third module (BuildPolyTSection) performs rasterization of each  $p, T$ -section and builds up the matrix as described in item 3 of algorithm, then receives information about boundaries of diagram phase fields from previous module.
- (4) Last one (ShowPolyTSection) makes graphical construction of obtained polythermal section.

Such modularization was made to divide the procedure of  $p, T$ -sections calculations and their analysis as well as to facilitate further modernization, addition of another functionality and integration with TernAPI.

It should be emphasized that quality of built polythermal section is essentially depends on defined temperature step  $\Delta T$ . It was emerged during program testing that optimal value of  $\Delta T$  is about 1% of temperature interval for diagram construction. Such  $\Delta T$  allows to find adequately most of existing phase fields of section and make the representation of obtained  $T$ - $x$ -diagrams in a user-friendly style.

Concerning operating time of the algorithm we can say that primary rate-controlling factor is the calculation of the isobaric-isothermal sections set. Depending on temperature and composition step it can take from a few minutes to hours on modern personal computer and amount to about 80% of program working time, where almost 2/3 of calculation time goes to the construction of convex hull and the remainder – to the determination of their phase compositions and boundaries. Remaining availability is taken by construction of the final  $T$ - $x$ -diagram (usually 5-60 seconds). Therefore we recommend begin with calculation and saving the set of  $p, T$ -sections for chosen system to improve the time for construction of arbitrary polythermal section loading it from outside.

Suggested algorithm tested on the next groups of systems:

- (1) Systems with ternary eutectic (model, LiF-LiCl-LiI etc.)
- (2) Systems with splitting solutions (model, CdTe-HgTe-ZnTe, Au-Pt-Pd etc.)
- (3) Systems with a large number of phases with non-permanent composition (Au-Bi-Sb, Al-Mg-Zn etc.)

An agreement between calculated diagrams and literature data confirms the applicability of the developed technique of polythermal sections assessment for a wide range of ternary systems. As an example the comparison between calculated and reference sections of ternary Au-Bi-Sb diagram with is shown on the Figure 1. Model descriptions for all phases in this system were taken from [3] and reference plotted polythermal section was taken from [4]. As can be seen calculated polythermal section contains phase fields boundaries of different colors. The reason for that will be described below.

During the algorithm testing a necessity to upgrade TernAPI program for improving accuracy in determination of phase boundaries around singular points of phase diagram (eutectic, peritectic, critical points etc.) was clearly shown.

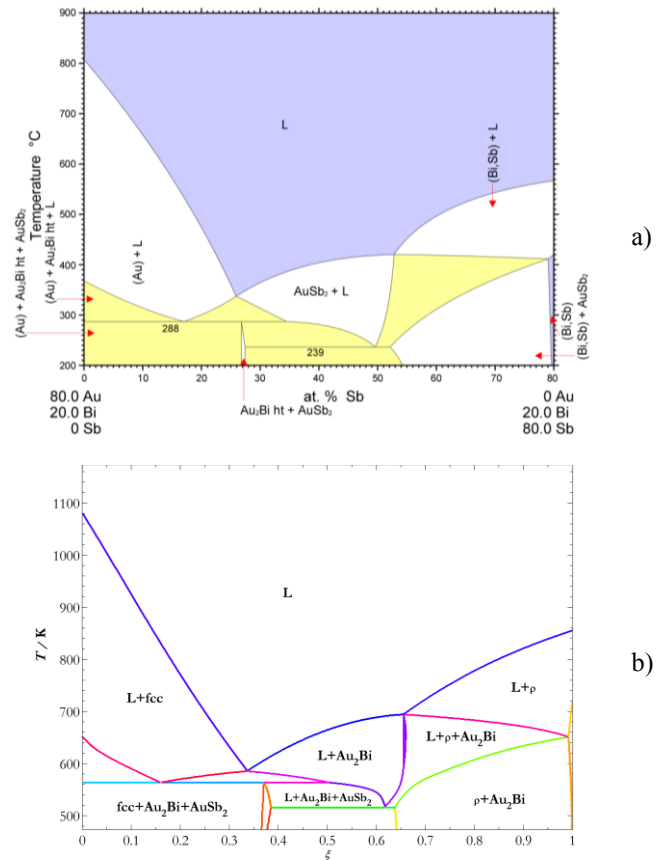


Figure 1. Polythermal section of Au-Bi-Sb phase diagram with constant molar fraction of Bi  $x_{Bi} = 0.2$ : a – from [4], b – calculated using suggested algorithm.

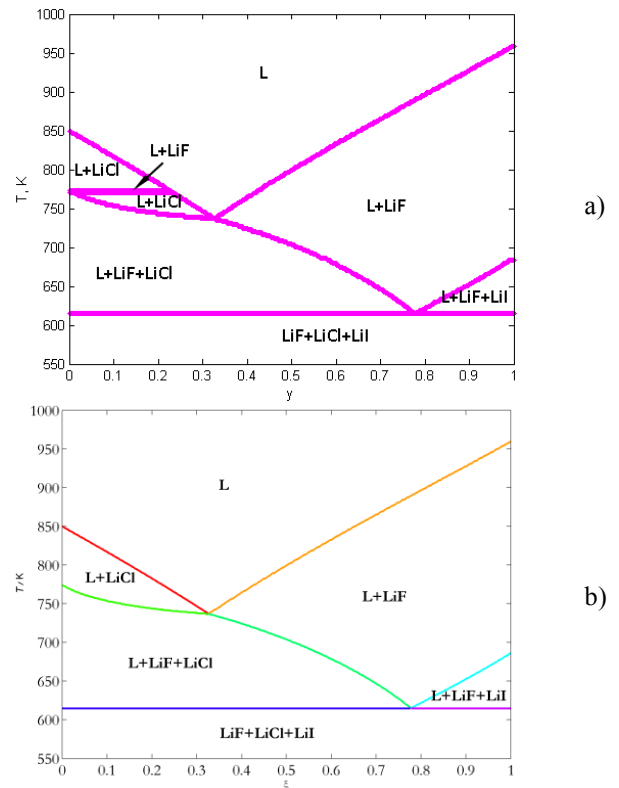


Figure 2. Polythermal section of LiF-LiCl-LiI phase diagram (0.9;0)-(0;0.5). Coordinates are given as  $(x_2^{start}, x_3^{start})-(x_2^{final}, x_3^{final})$ . a – first version of program, b – calculated using refined algorithm.

To illustrate this an arbitrary polythermal section in the ternary LiF-LiCl-LiI diagram is shown on Figure 2a. Model description for this system was taken from [5] and [6]. One can see the splitting of one whole two-phase region L+LiCl into two due to “wedging” between them of narrow two-phase band L+LiF. Such inaccuracy is caused by the problems of discrimination between three- and two-phase diagram regions. As can be seen on the Figure 3, narrow three-phase triangle near the eutectic point is incorrectly recognized as two-phase. Such error distorts the view of polythermal section; it is caused by the convex hull projection analysis algorithm features (which is based on geometrical principles) used in TernAPI.

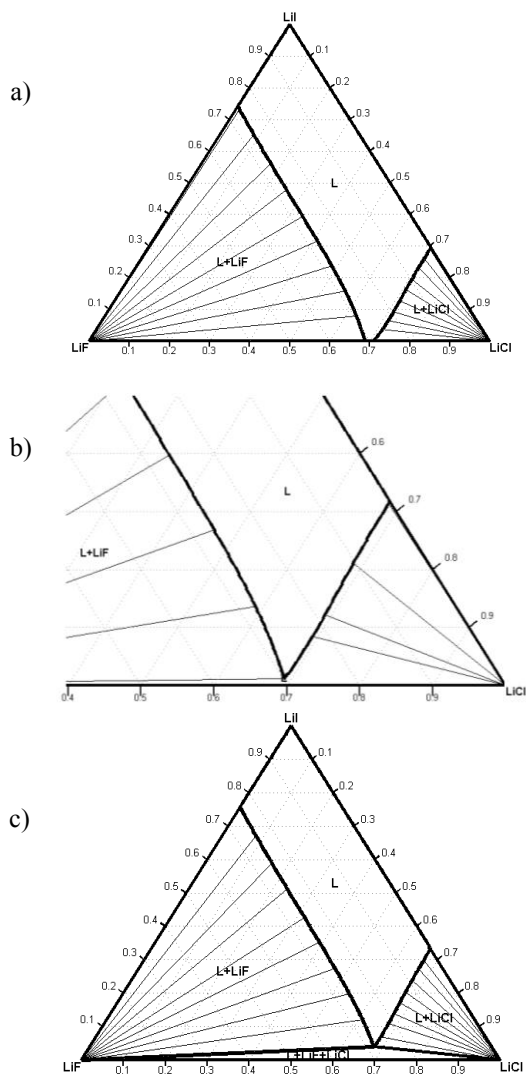


Figure 3. Calculated isothermal sections of LiF-LiCl-LiI phase diagram at: a – 779 K, b – 771 K, c – 765 K.

It can be avoided by decreasing composition step that results in increasing of the section calculation and visualization time. Another possible way is in comparing two  $p, T$ -sections differed from each other by the value of  $\Delta T$  in temperature with further recognition and automatic repairing the “artefacts”, but this method takes additional investigations and significant sophistication of the algorithm. We used different approach.

This one and other corrections of algorithm implementation drawbacks mentioned above are described in the next section of this article.

## ALGORITHM REFINEMENT

In the new version of algorithm some its parts were significantly improved. The most important features are the follows:

- (1) Inaccuracy in determination of phase boundaries around singular points of phase diagram was eliminated by the modification of TernAPI kernel.
- (2) Combining of single points dividing phase diagrams into a solid lines of phase boundaries was added.
- (3) Time of polythermal section construction from precalculated set of  $p, T$ -sections was reduced to one-tenth as much (now it is less than 10 sec on a typical modern personal computer).

Elimination of errors in phase boundaries determination near singular points was achieved by addition of extra procedure of phase number assessment inside the triangles of the convex hull projection to the  $(x_2, x_3)$  plane. It was made by the modification of TernAPI kernel. Old version of algorithm includes only one method of its assessment based on geometrical properties of the triangles [2]. Extra procedure contains two steps:

- (1) Calculate number of phases by counting the number of Gibbs energy functions (points, lines, surfaces) touched by the triangle.
- (2) Use obtained number of phases if it is greater that calculated by the geometrical method

In this technique geometrical method allows to detect miscibility gaps generated by the one phase (e.g. liquid) and non-geometrical method can discriminate between three and two-phase region near such singular points as eutectic and peritectic.

New feature of program to determine phase regions boundaries not as dotted but solid improves the visual appearance of phase diagrams and makes its automatic analysis easier (e.g. during thermodynamic model parameters optimization based on an experimental data set). It can be seen on Figures 2b and 3b, where boundaries dividing different fields have distinct colours. Comparing Figures 3a and 3b one can see also developments of the algorithm in second version vs first one.

Algorithm performance improvement was achieved by means of program code optimization that includes MATLAB code refactoring and rewriting of its critical parts (from the viewpoint of performance) to the C programming language. Comparison of two program versions performance is shown in the Table 1.

Table 1. Comparison of the algorithm performance before and after optimization.

Section assessment stage	Time elapsed, relative units <sup>a</sup>	
	Before optimization	After optimization
Convex hulls construction	1	1
$p, T$ -sections analysis	0.64	0.42
Polythermal section construction	0.05	0.0035

<sup>a</sup> “Relative unit” is time elapsed on the convex hull construction that was not changed after optimization

## DISCUSSION OF THE RESULTS

The algorithm of ternary systems polythermal sections calculation has been proposed and refined in the present work; and its efficiency and robustness during testing was clearly shown. Its key feature is preliminary calculation of  $p, T$ -sections array by the convex hull method with the fixed step  $\Delta T$  between them. Although such procedure requires a lot of time (about 5-60 minutes on the modern personal computers) it allows further rapid (in several seconds) polythermal section construction that can be useful for the phase diagram exploration. The process of calculation can be easily parallelized on the multicore/multiprocessor computer. Obtained  $p, T$ -sections array also makes possible a fast visualization of three-dimensional boundaries (i.e. surfaces) between regions of polythermal phase diagram (e.g. liquidus or solidus surface).

The geometrical approach that is the basis of the developed algorithm (see “polythermal sections construction method” section) can be generalized to the isothermal and polythermal sections of the multicomponent systems (e.g. quaternary). Another way of improvement is the minimization of convex hull construction elapsed time. It may be achieved by an adaptation of existing convex hull building algorithms for a phase diagram assessment task. For the case of binary systems such approach been described in the literature [7].

## CONCLUSIONS

In the present work an effective algorithm for the ternary phase diagrams polythermal sections assessment based on the convex hull method has been proposed and successfully tested. Although it's significantly slower than the algorithms based on the Gibbs energy minimization in the case of single polythermal section calculation, it has an important advantage over it: after assessment of one polythermal section the next ones can be obtained almost instantly.

Possible ways of further development of the proposed algorithm are its generalization for the multicomponent system case and increasing its performance by the optimization of  $p, T$ -sections array assessment.

## ACKNOWLEDGMENT

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## NOMENCLATURE

Symbol	Quantity	SI Unit
$G$	Gibbs energy	$\text{J}\cdot\text{mol}^{-1}$
$n_i$	Amount of i-th component	mol
$V$	Volume	$\text{m}^3$
$p$	Pressure	bar
$T$	Temperature	K
$x_i$	Mole fraction of i-th component	
$\xi, y$	Coordinate on section line proportional to mixture composition	

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